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**ARL-RP-94**

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## Fatty acid-based monomers as styrene replacements for liquid molding resins

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### Abstract

One method of reducing styrene emissions from vinyl ester (VE) and unsaturated polyester resins (UPE) is to replace some or all of the styrene with fatty acid-based monomers. Methacrylated fatty acid (MFA) monomers are ideal candidates because they are inexpensive, have low volatilities, and free-radically polymerize with vinyl ester. The viscosity of VE resins using these fatty acid monomers ranged from 700–2000 cP, which is considerably higher than that of VE/styrene resins ( $\sim 100$  cP). In addition, the  $T_g$  of VE/MFA polymers were only on the order of 80 °C, which is significantly lower than that of VE/styrene polymers. Decreasing the length of the base fatty acid chains from 18 to 12 carbon atoms improved the  $T_g$  by 20 °C, while lowering the resin viscosity from  $\sim 2500$  to  $\sim 1000$  cP. Residual unsaturation sites on the fatty acid backbone decreased the cure rate of the resins thereby decreasing polymer properties. Ternary blends of VE, styrene, and fatty acid monomers also effectively improved the flexural, fracture, and thermo-mechanical properties and reduced the resin viscosity to acceptable levels, while using less than 15 wt% styrene, far less than commercial VE resins.

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**Keywords:** Fatty acid monomers; Styrene replacements/alternatives; Vinyl esters

### 1. Introduction

Vinyl ester (VE) and unsaturated polyester (UPE) resins are used to make polymer matrix composites in military and commercial applications because of their good properties, low weight and low cost. These resins typically contain high concentrations of reactive diluents, such as styrene, to allow these resins to be molded using resin transfer molding and other inexpensive liquid molding techniques. Because styrene is a hazardous air pollutant (HAP) and a volatile organic compound (VOC), the Federal Environmental Protection Agency of the United States of America introduced legislation to limit styrene emissions from composite manufacturing [1]. Therefore, non-volatile reactive diluents, such as fatty acid (FA) monomers, offer a large advantage over current reactive diluents.

There are a number of reasons why the study and development of fatty acid-based monomers for use in liquid molding resins is important. First of all, fatty acid monomers can be used to replace some or all of the styrene used in liquid thermosetting resins. Fatty acid monomers are excellent alternatives to styrene because of their low cost and low volatility. In addition, fatty acids are renewable resources because they are derived from plant oils. Therefore, not only would the use of fatty acids in liquid molding resins reduce VOC emissions, thereby reducing health and environmental risks, but it also would promote global sustainability.

Fatty acid monomers are derived from plant oils, such as soybean oil, which are composed of over 99% triglyceride molecules [2]. Triglycerides are composed of three fatty acids connected by a glycerol center. The triglycerides in plant oils typically contain 10 or more different fatty acids, which range in length, level of unsaturation, and functionality (e.g. epoxide and hydroxyl functionality as found in vernonia and castor oils, respectively) [2].

Fatty acids and triglycerides have been used in a number

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of polymeric applications. Epoxidized and acrylated triglycerides have been used as plasticizers and toughening agents [3]. In fact, the largest non-food use of triglycerides is the use of epoxidized soybean and linseed oils as plasticizers in poly(vinyl chloride) [3]. Pressure sensitive adhesives have been made from fatty acid methyl esters [4]. In addition, thermosetting liquid molding resins, similar to VE resins, have been made using plant oils as the cross-linkers [5–7]. However, until now, fatty acids have not been used as reactive diluents in thermosetting liquid molding resins.

Although it is imperative to reduce styrene emissions from VE and UPE resins, the processing of these resins and their resulting polymer properties must be similar to that of commercial VE. Therefore, viscometric, thermal and mechanical characterization of the resulting resins and polymers must be done to assess the ability of fatty acid monomers to replace some or all of the styrene in liquid molding resins.

## 2. Experimental

### 2.1. Vinyl ester preparation

Vinyl ester monomers were prepared via methacrylation of diglycidyl ether of bisphenol A (DGEBA) [8] (Fig. 1) catalyzed using AMC-2 (Aerojet Chemicals, Rancho Cordova, CA), which is a mixture of 50% trivalent organic chromium complexes and 50% phthalate esters [9]. Epon 828 (Miller Stephenson, Danbury, CT.) ( $n=0.098$ ) was used as the DGEBA, and its methacrylated analog is dubbed VE 828. The effect of VE molecular weight on the properties of VE/FA resins was not tested, but will be used in the future to optimize the resin system.

### 2.2. Vinyl ester characterization

Acid number titration was used to measure the amount of free (unreacted) acid in the VE system [10]. Approximately 1 g of the VE reaction mixture was dissolved in 5 g acetone.

Three drops of 0.5 wt% phenolphthalein in 50% ethanol were added to the mixture to determine the neutralization point. The solution was then titrated with 0.5 N sodium hydroxide until the solution remained slightly pink in color for 30 s. An acid number (mg NaOH/g VE) of 10, corresponding to  $\sim 3\%$  free acid, was the maximum allowable acid number. If the acid number was too high, the methacrylation reaction was allowed to continue until future acid numbers were below 10.

Fourier Transform Infrared Spectroscopy (FTIR) was used to measure the concentration of unreacted epoxides and attached methacrylate groups. A Thermo Nicolet Nexus 670 FTIR was used in absorbance mode, taking 16 scans per spectrum with a resolution of  $4\text{ cm}^{-1}$ . The FTIR spectra of these resins indicated that all of the epoxide groups ( $917\text{ cm}^{-1}$ ) reacted [11], and methacrylate groups ( $942\text{ cm}^{-1}$ ) [12] were present in the resin.

Size exclusion chromatography (SEC) was run on the VE samples to determine if extensive methacrylation and/or epoxy homopolymerization occurred. A Waters 515 GPC was used with two  $5\text{ }\mu\text{m}$  styrene-divinyl benzene columns in series. The columns were equilibrated and run at  $45\text{ }^{\circ}\text{C}$  using tetrahydrofuran (THF) (Aldrich, Milwaukee, WI) as the elution solvent at a flow rate of  $1\text{ mL/min}$ . The column effluent was monitored by two detectors operating at  $25\text{ }^{\circ}\text{C}$ : a Waters 2410 refractive index detector and a Waters 2487 dual absorbance detector operating at 270 and 254 nm (absorbed by phenyl rings). Samples were prepared by dissolving 2 mg sample in 1 mL THF. Because high molecular weight species cannot diffuse into the packing, they elute first from the column, while lower molecular weight species elute later [13].

The SEC chromatographs for Epon 828 has two peaks. The small peak at 14.5 min represents Epon with two bisphenol units ( $n=1$ ) while the large peak at 15.5 min represents the Epon with one bisphenol unit ( $n=0$ ). After reaction with methacrylic acid, these peaks shift to earlier times (13.75 and 14.5 min), indicating that the methacrylic acid has added to the Epon. Previous work has shown that if a significant amount of epoxy homopolymerization occurred, a broad peak appearing at approximately 10 min

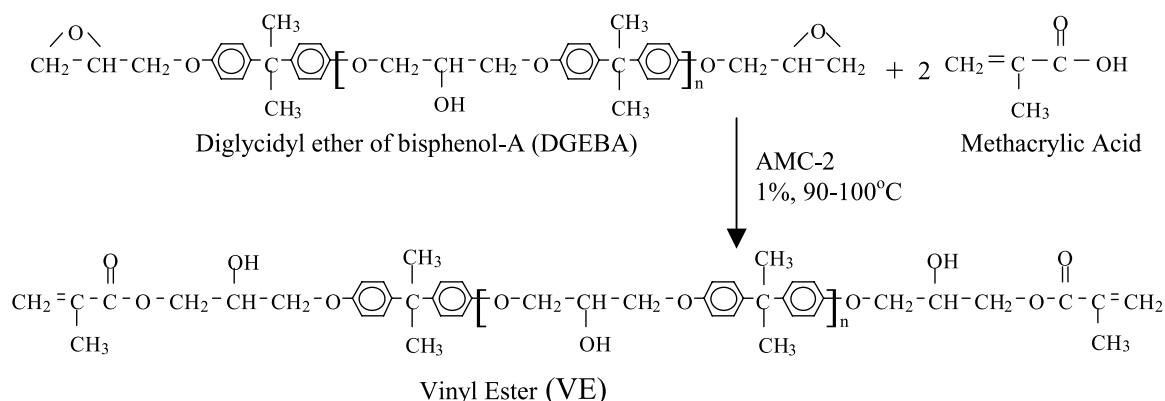


Fig. 1. The reaction of methacrylic acid with DGEBA to form vinyl ester monomer.

would appear [6,13]. Because no such peak appeared in our prepared vinyl esters, we concluded that no epoxy homopolymerization occurred. In addition, these results conclusively showed that Epon reacted with the methacrylic acid to form higher molecular weight vinyl ester monomers.

### 2.3. Fatty acid monomer preparation

A number of synthetic procedures have been established for making fatty acid-based monomers to be used as the reactive diluent in VE resins [14]. Fig. 2 depicts the synthetic route used to form the methacrylated fatty acids (MFA). The carboxylic acid of fatty acids undergoes a simple addition reaction with the epoxide group of glycidyl methacrylate (Aldrich, Milwaukee, WI) to form a single product. Stoichiometric quantities of the reactants were mixed together and reacted at 70°C for 2.5 hrs using 1 wt% AMC-2 catalyst. FTIR and  $^1\text{H}$  NMR (250.13 MHz, spectral window of  $\pm 2000$  Hz, 0.427 Hz/pt digital resolution, 16 scans at 293 K, 90° pulse width) with a Bruker (Billerica, MA) AC250 Spectrometer showed that methacrylation of the fatty acids went to completion. Each MFA contains one terminal polymerizable unsaturation site per molecule. In this way, the fatty acid monomers act as chain extenders, analogous to styrene, in VE resins. The MFA is a fairly long hydrocarbon typically ranging in length from 20 to 26 atoms, depending on the fatty acid used. The length of the fatty acid chain may affect the polymer properties. In addition, plant oils typically contain mixtures of saturated and unsaturated fatty acids, which also may affect the polymer properties. Therefore, the particular fatty acid used is of importance, and its effect on polymer properties has been studied. Four fatty acids were used to determine the effect of fatty acid structure on resin and polymer properties: lauric acid (Lau) (Sigma, St Louis, MO.), stearic acid (SA), oleic acid (OA) (Fisher Scientific, Fair Lawn, NJ), and linoleic acid (Lin) (Sigma, St Louis, MO.). The molecular structure differences of these fatty acids are summarized in Table 1. The choice of these fatty acids allowed us to determine the effect of fatty acid length and unsaturation level on resin and polymer properties.

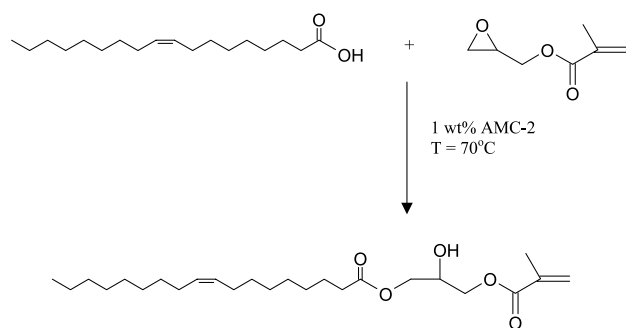


Fig. 2. The addition of fatty acids (oleic acid) to glycidyl methacrylate to form methacrylated fatty acid monomer (patent pending).

Table 1

The molecular structure differences of the fatty acids used to prepare MFA monomers

Fatty acid	Chain length in carbon atoms	Unsaturation sites
Lauric acid	12	0
Stearic acid	18	0
Oleic acid	18	1
Linoleic acid	18	2

### 2.4. Monomer viscosity

The viscosities of the fatty acid monomers and resins were measured using a Brookfield digital viscometer in Couette geometry (concentric cylinders) [15]. Approximately 8 ml of the sample were placed into the sample holder. The appropriate spindle and shear rate were selected to maximize the allowable torque. All samples were run at 30 °C.

### 2.5. Resin cure

VE resins containing 35 and 45 wt% fatty acid monomers were prepared. The resins were cured at room temperature using a mixture of trigonox 239A (Akzo Nobel Chemicals, Chicago, IL), containing 45% cumene hydroperoxide, and cobalt naphthenate (CoNap). The trigonox and CoNap (Aldrich, Milwaukee, WI) masses used were 1.5 and 0.375%, respectively, of the total resin mass. Methacrylated stearic acid (MSA) was not cured with VE at room temperature because MSA is a solid at this temperature even when mixed with VE monomers. The resins were also cured at 90 °C using only 1.5 wt% Trigonox (no CoNap) to test the effect of elevated cure temperatures. Derakane 411-C50 (Dow, Midland, MI) was also cured using 1.5 wt% trigonox and 0.375 wt% CoNap to compare fatty acid-based resins to commercial resins.

Ternary VE resins were prepared using VE monomer, MFA, and styrene. These resins contained 65 and 55 wt% vinyl ester monomer. The balances of the resins were made up of MFA and styrene, and the content of each reactive diluent was varied from 0 to 100% of the balance. The resins were cured at room temperature using 1.5 wt% Trigonox and 0.375 wt% CoNap.

### 2.6. Cure kinetics

VE was cured in the presence of 35 and 45 wt% of the various MFA monomers to determine the effect of fatty acid structure on cure kinetics. In addition, MFA were homopolymerized to eliminate the effect of VE on the polymerization reaction. For comparison purposes, VE was cured with styrene. The cure kinetics of ternary mixtures of VE, MFA and styrene were also measured.

A Nicolet Magna 860 Fourier FTIR operating in transmission mode with 4  $\text{cm}^{-1}$  resolution was used. The

set-up of the FTIR cell is explained elsewhere [12]. A drop of the resin was sandwiched between two 25 mm diameter NaCl disks (International Crystal Labs) separated by a 0.025 mm thick Teflon™ spacer (International Crystal Labs). One sodium chloride disk was 2 mm thick while the other was 4 mm thick. The salt plate assembly was placed in a cell holder. The temperature of the cell holder can be controlled to within  $\pm 0.1$  °C of the set-point. When the cell holder equilibrated to 90 °C, the salt plate assembly was placed in the holder, and the first FTIR scan was taken. All resin mixtures were cured at 90 °C for 4 h and post-cured at 120 °C for an additional 2 h. An FTIR spectrum comprised of 16 scans was taken every 30 s during the cure reaction.

The conversion,  $\alpha$ , was calculated by measuring the height of the peak relative to an internal standard (i.e. a group that is not affected by the reaction) (Eq. (1)):

$$\alpha = 1 - \left( \frac{\text{ABS}(t)_{\text{peak}}}{\text{ABS}(t=0)_{\text{peak}}} \right) \left( \frac{\text{ABS}(t=0)_{\text{standard}}}{\text{ABS}(t)_{\text{standard}}} \right) \quad (1)$$

The cure kinetics were fit to an autocatalytic model [12]. Both VE monomers and MFA contain methacrylate groups that appear at  $942 \text{ cm}^{-1}$ . The methacrylate conversion was calculated by measuring the height of the peak relative to the vinyl ester aromatic C–H stretch at  $828 \text{ cm}^{-1}$  [12,16]. The styrene conversion was calculated by measuring the styrene carbon–carbon double bond peak height ( $910 \text{ cm}^{-1}$ ) relative to the styrene aromatic C–H stretch ( $700 \text{ cm}^{-1}$ ) [12,16]. To resolve the cure of VE from the cure of the MFA, acrylated vinyl ester was prepared. Acrylated vinyl ester was prepared in the same way as methacrylated vinyl ester, except acrylic acid was used rather than methacrylic acid in the synthesis procedure (Fig. 1). Acrylate groups appear at  $990 \text{ cm}^{-1}$  [11]. The disappearance of the acrylate peak and the methacrylate peak relative to the vinyl ester internal standard was used to calculate the cure rate of the individual components.

### 2.7. Polymer properties

The thermo-mechanical properties of vinyl esters were measured using dynamic mechanical analysis (DMA). Rectangular samples with approximate dimensions of  $25 \times 9 \times 3 \text{ mm}^3$  were tested using a TA Instruments 2980 DMA in single cantilever geometry. The samples were tested at 1 Hz with a deflection of  $15 \mu\text{m}$  while ramping the temperature from 30 to 200 °C at a rate of 5 °C/min. Three temperature ramp experiments were run for each sample. The first ramp usually completely post-cured the polymer, but another ramp was performed to ensure this. The temperature at which the peak in the loss modulus occurred in the fully post-cured polymer was considered the glass transition temperature of the material [17]. The point at which the modulus in the rubbery plateau began to increase with increasing temperature was used to calculate the

molecular weight between cross-links,  $M_c$ . The theory of Rubber Elasticity was used to calculate  $M_c$  (Eq. (2)):

$$E = 3RT\rho/M_c \quad (2)$$

where  $E$  is the rubbery modulus,  $R$  is the ideal gas constant,  $T$  is the absolute temperature, and  $\rho$  is the sample density [18,19].

Flexural tests were performed to determine the modulus of elasticity and flexural strength in accordance with ASTM D790-92, Test Method I, Procedure A [20]. The samples had dimensions of  $130 \times 13 \times 3 \text{ mm}^3$  and were tested flat-wise on a support span, resulting in a support-to-depth ratio of 16. The samples were tested using an Instron 5500R at a crosshead speed of 0.5 in./min. All tests were performed at 22–23 °C and 20–25% relative humidity.

Three-point single-edge notch bend (SENB) specimens were used for fracture toughness measurements [21]. The sample dimensions were  $2.00 \times 0.50 \times 0.25 \text{ in.}^3$  to assure plain strain conditions. An initial crack was made by notching the specimens a distance of half their depth. A sharp razor blade was used to initiate a crack at the base of the notches. The samples were tested using an Instron 4505 in flexural mode at a crosshead speed of 0.05 in./min. An unnotched sample was run in the same manner twice during the course of the experiment to account for system compliance, loading pin penetration, and sample compression. All tests were performed at 22–23 °C and 20–25% relative humidity. When tests were completed, the fracture specimens were examined for signs of plastic deformation. If plastic deformation was apparent, the sample was not used in the reported results.

## 3. Results and discussion

### 3.1. Monomer and resin viscosity

The viscosities of the MFA and the reactants used to produce these monomers were measured at 30 °C using a Brookfield digital viscometer. The viscosities of oleic acid and linoleic acid were 24 cP (lauric acid and stearic acid are crystalline solids at 30 °C), while the viscosity of glycidyl methacrylate was  $\sim 1$  cP. The viscosities of MFA monomers (Table 2) were higher than their starting materials because MFA contain hydroxy-ester groups, which induce hydrogen bonding [22,23]. The viscosities of the VE resins before cure are also shown in Table 2. The viscosities of MFA resins increased with chain length and as the level of unsaturation along the fatty acid backbone decreased. The level of unsaturation affected the viscosity because these sites put kinks along the fatty acid chain that increase the intermolecular spacing [24], thereby reducing intermolecular interactions and the viscosity. These results show that MLau is the best fatty acid monomer for making low viscosity resins for liquid molding. However, the viscosities



Table 2

The initial viscosity at 30 °C of methacrylated fatty acids and VE resins using these monomers as a diluent

Comonomer	Fatty acid properties chain length (carbon atoms): unsaturation sites	Viscosity (cP)		
		100% Comonomer	35% Comonomer	45% Comonomer
MLau	12:0	48	1720 ± 4	792 ± 4
MSA	18:0	N.A.	N.A.	N.A.
MOA	18:1	58	2720 ± 4	2000 ± 4
Mlin	18:2	56	2500 ± 4	1900 ± 4
Styrene	N.A.	0.7	95 ± 4	35 ± 4

The viscosity of methacrylated stearic acid was not measured because MSA is a solid, even when mixed with VE monomer.

of its VE resins are considerably higher than that of VE/styrene resins because FA monomers have considerably higher viscosities than styrene.

The viscosities of VE resins using MFA were fairly high. To reduce the viscosity, blends of MFA and styrene were used as the reactive diluent in VE 828. The viscosity of VE/MFA/styrene was measured at 30 °C and was found to decrease exponentially with styrene content for resins containing 55 and 65 wt% VE 828 resin (Fig. 3, shown for MLau-based resins). Styrene contents of less than 10% reduced the viscosity of VE resins to the acceptable range (< 500 cP) [25,26]. Therefore, only low styrene contents are necessary, from a viscosity point of view.

### 3.2. Cure kinetics

The cure rate decreased as the number of residual unsaturation sites on the fatty acid backbone increased (Fig. 4). Furthermore, the ultimate conversion decreased as a result of these residual unsaturation sites. The unsaturation sites on fatty acid backbones are similar to allyl groups. It has been shown that allyl groups do not free-radically polymerize [27,28]. Instead, chain transfer to allyl groups occurs [28]. Allyl radicals are too stable to initiate polymerization and essentially act as inhibitors [27,28].

Therefore, the unsaturation sites on the fatty acid backbone were expected to reduce the cure rate. These effects were more pronounced for the homopolymerization of MFA because of increased concentration of MFA monomers. On the other hand, fatty acid chain length was not found to have any effect on VE cure kinetics. Therefore, MFAs based on lauric acid or stearic acid are ideal for achieving fast cure rates and high extents of cure, which should result in improved polymer properties.

The cure rates of all MFA resins, except linoleic acid based monomers, were higher than that of styrene-based resins (Fig. 4). This effect is a result of the fact that VE/styrene blends vitrify at a much lower temperature than VE/MFA blends because of the greater amount of free volume introduced from the MFA. In addition, the presence of inhibitor in the styrene could decrease the cure rate of VE/styrene. The overall conversion of VE/MFA resins was slightly lower than VE/styrene resins, due to the continuing polymerization of styrene even after VE polymerization is done because of styrene's high mobility (i.e. low molecular weight and compact size) in a gelled resin [16]. Ternary blends of VE, MFA and styrene had cure rates and extents of cure that were higher than both VE/MFA and VE/styrene alone (Fig. 5). The lower  $T_g$  of the fatty acid zones allows

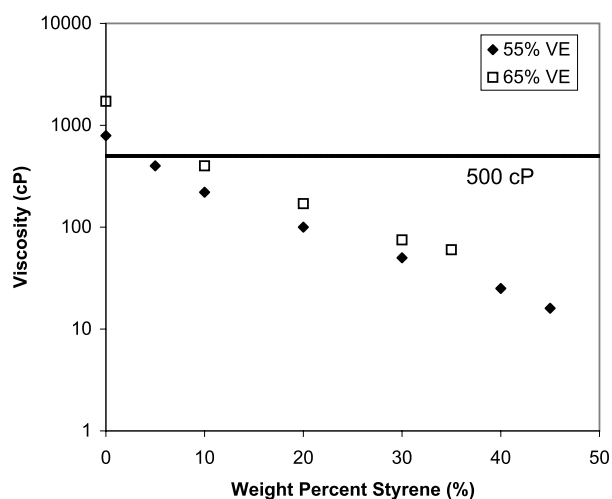


Fig. 3. The viscosity of VE/MLau/styrene as a function of styrene content in the resin for resins containing 55 and 65 wt% VE 828.

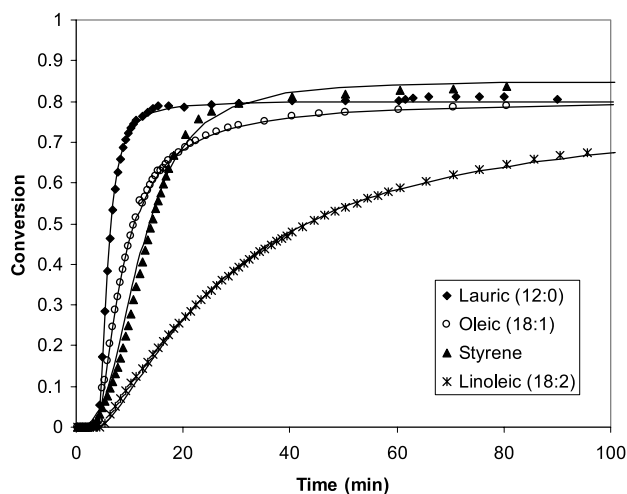


Fig. 4. The conversion as a function of time for the cure of VE/MFA relative to VE/styrene and their autocatalytic fits using 45% reactive diluent. Samples were cured at 90 °C.

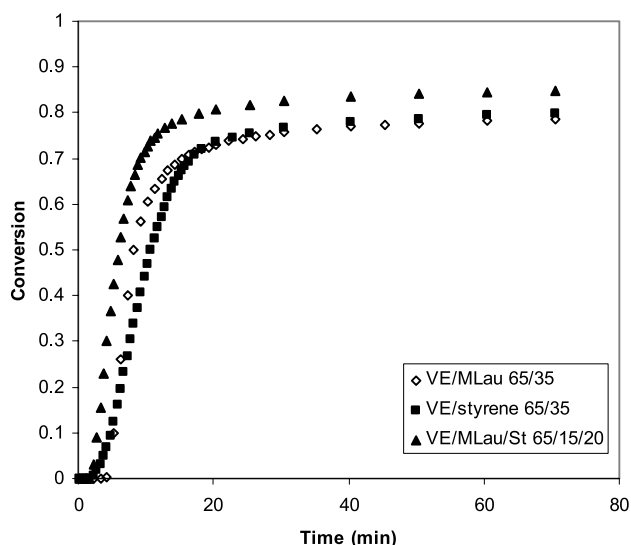


Fig. 5. The conversion as a function of time for the cure of VE/MLau/Styrene 65/15/20 relative to VE/MLau 65/35 and VE/styrene 65/35 and their autocatalytic fits. Samples were cured at 90 °C.

for greater mobility of styrene in the polymer, enabling it to almost completely react into the polymer network. The greater cure rate for the ternary blend is a result of a lower vitrification temperature than VE/styrene along with higher monomer mobility than VE/MFA.

Using the acrylated vinyl esters (VEA), the conversion of the individual monomers was observed. It was found that the VE monomers of VE/MFA reacted to a high extent (85%), while the MFA only reacted to ~65%. This is in contrast to VE/styrene resins, where the VE only reacts to 70% while styrene reacts to >90% [16]. We hypothesize that vinyl ester monomers cure to a high extent in MFA resins because the long side groups of MFA allow for flexibility of the network and reduce diffusion limitations to growing polymer chains. MFA react to a low extent because of the inherent low reactivity of methacrylate groups with themselves relative to the vinyl group of styrene [29]. In addition, it is possible that MFA monomers phase separate into micro domains because they are chemically different from VE monomers [16]. This would reduce the accessibility and thereby reactivity of the MFA methacrylate groups.

Table 3

The properties of styrene and fatty acid based vinyl esters cured at room temperature and post-cured with a temperature ramp from room temperature to 200 °C at 5 °C/min

Comonomer	35% Comonomer			45% Comonomer		
	$T_g$ (°C)	$E'$ at 35 °C (Mpa)	$M_c$ (g/mol)	$T_g$ (°C)	$E'$ at 35 °C (Mpa)	$M_c$ (g/mol)
Styrene	147	2.9	328	142	2.6	642
Mlau	79	2.0	211	71	1.5	304
MOA	76	1.6	240	75	1.1	373
Mlin	72	1.6	290	69	1.0	400

### 3.3. Polymer properties

Thermo-mechanical properties were measured using DMA. Polymers using MFA monomers produced hard and rigid polymers, similar to that of commercial VE polymers. Table 3 lists the properties of the VE/MFA polymers cured at room temperature and then post-cured with a 5 °C/min temperature ramp from room temperature to 200 °C. The moduli were greater than 1 GPa. DMA shows that  $T_g$  was less than 100 °C for these polymers. Both  $T_g$  and the modulus increased as the fatty acid chain length decreased. This was expected because longer fatty acid chains increase the free volume of the polymer and increase the effective molecular weight between cross-links. The glassy modulus and  $T_g$  decreased as the level of unsaturation of the fatty acid chain increased. This is clearly visible for the MLin samples, which had moduli of 20% lower and  $T_g$  of 15 °C lower than the other MFA monomers. This is consistent with the fact that MLin monomers cured the slowest and to the lowest extent of the MFA monomers tested.

The rubber moduli of the polymers were ~45 MPa, indicating the molecular weight between cross-links,  $M_c$ , was 200–300 g/mol, as per Eq. (2). For fatty acids with chain lengths of 18 carbon atoms,  $M_c$  should be 280 and 300 g/mol for 35 and 45% MFA comonomer, respectively, which is in good agreement with our results.  $M_c$  decreased as the fatty acid chain length decreased, as expected (Table 3).

Curing the resins at elevated temperature increased the polymer properties (Table 4). Comparing Tables 3 and 4, it is obvious that both  $T_g$  and the modulus increased while  $M_c$  decreased as the cure temperature increased. These results were expected because elevated cure temperatures typically increase the extent of cure [16].

Ternary blends of VE, MFA, and styrene were used to improve the thermo-mechanical properties relative to VE/MFA resins while having lower VOC emissions. The DMA character of these ternary resins improved as the styrene content increased, as shown in Fig. 6 for VE/MOA/styrene blends. The storage modulus at a given temperature and the temperature at which the peak in the loss modulus occurred increased as the styrene content in the ternary blend increased. In addition, the maximum loss modulus value decreased as the styrene content decreased, indicating

Table 4

The properties of MFA-based vinyl esters cured at 90 °C and then post-cured with a temperature ramp from room temperature to 200 °C at 5 °C/min

Comonomer	35% Comonomer			45% Comonomer		
	$T_g$ (°C)	$E'$ at 35 °C (GPa)	$M_c$ (g/mol)	$T_g$ (°C)	$E'$ at 35 °C (GPa)	$M_c$ (g/mol)
Styrene	150	3.0	297	145	2.7	432
MLau	94	1.9	213	77	1.6	321
MSA	93	1.65	206	84	1.2	299
MOA	90	1.7	164	76	1.3	275
MLin	79	1.6	218	69	1.2	335

that the glass transition broadened as the MFA content increased. Fig. 7 shows that  $T_g$  improved in a linear fashion with increasing styrene content. These results show that 15% styrene is sufficient to obtain an acceptable modulus and  $T_g$  for MOA blends, while 10–15% is sufficient for MLau blends because of the higher physical properties of MLau polymers relative to MOA polymers (Tables 3 and 4). Furthermore, at these styrene contents, the resin viscosity is well within the acceptable window for vacuum infusion and other traditional composite infusion methods.

Fig. 8 shows the flexural properties as a function of styrene content in the resin. When using MFA as the only reactive diluent, the physical properties are considerably lower than that of styrene-based vinyl ester resins. Replacing some of the styrene with MFA results in properties intermediate between MFA-based and styrene-based resins. For samples with 35% reactive diluent, the flexural strength increased from 83 MPa (VE/MLau) to 134 MPa (VE/styrene), while the flexural modulus increased from 2.59 GPa (VE/MLau) to 4.02 GPa (VE/styrene). This property improvement was larger for samples with 45% reactive diluent as the flexural strength increased from 61 to 139 MPa and the modulus increased from 1.9 to 3.9 GPa as the styrene content in the ternary blend increased. In all cases, the flexural strength and moduli of the ternary systems were slightly greater than a linear

increase. This is due to the fact that ternary blends have a higher extent of cure than their binary counterparts. Only 10% styrene is required in the ternary blends to increase the flexural modulus to 3 GPa and the flexural strength to 100 MPa or greater. Therefore, using MFA to replace some styrene in VE resins still results in good flexural properties, while significantly reducing styrene emissions. In addition, Derakane 411-C50 was found to have similar flexural strength and modulus as found in the literature (3.4 GPa and 145 MPa) [30], and its properties are also similar to VE 828 with 45 wt% styrene (Fig. 8). The maximum strain was not a strong function of the reactive diluent used. The maximum strain increased from 4% to only 5% as the styrene content increased from 0 to 45 wt%.

The flexural properties of MLau-based vinyl esters are slightly greater than that of MOA-based vinyl esters. This was expected because of the shorter chain length, and thus, higher cross-link density of MLau. The largest flexural properties difference was for the VE/MFA binary blends, and the difference decreased as more of the MFA was replaced with styrene. The flexural strength of MLau-based ternary and binary blends ranged from 4 to 12% greater than MOA resins. The effect of fatty acid chain length on the flexural modulus was smaller. The modulus was only 1–10% greater for MLau resins relative to MOA resins.

The fracture properties of fatty acid based vinyl esters

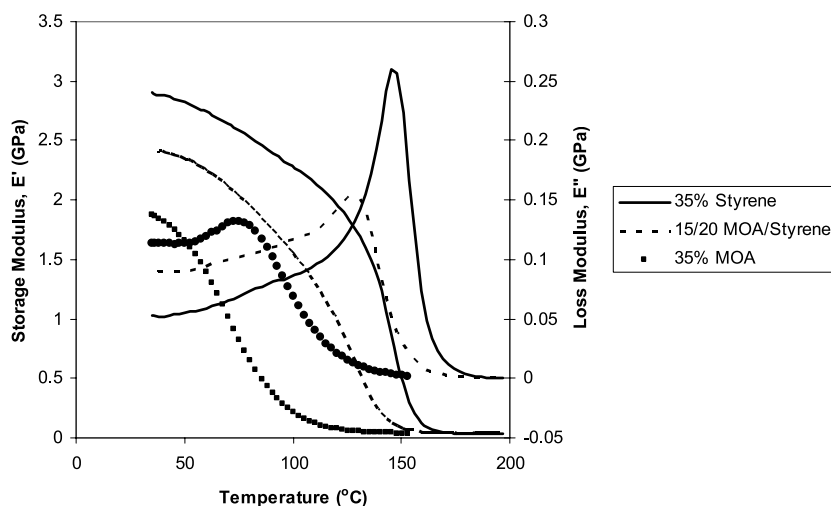


Fig. 6. DMA behavior of VE/MOA/styrene with 65 wt% VE 828. The loss modulus ( $E''$ ) curves go through a maximum, while the storage modulus ( $E'$ ) curves decrease monotonically as the temperature increases.

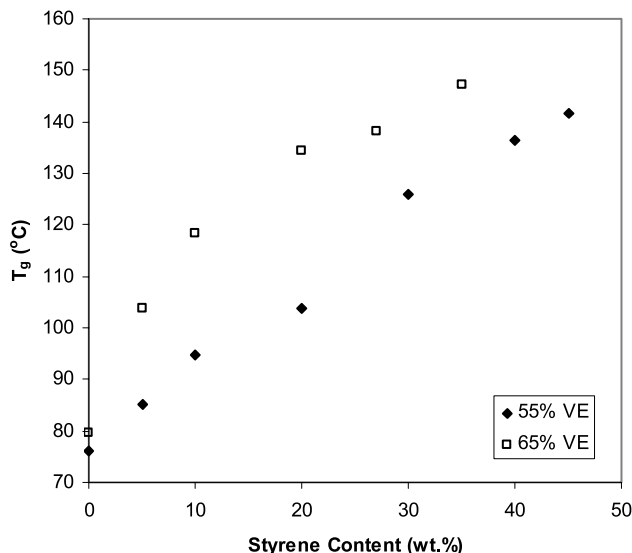


Fig. 7.  $T_g$  as a function of styrene content for VE/MLau/styrene blends.

depends on the structure of the fatty acid monomer. In all cases, methacrylated lauric acid-based resins had the best fracture properties, while methacrylated oleic and linolenic acid-based resins had the worst properties. For example, for resins with 35% reactive diluent, methacrylated lauric acid-based resins had a  $G_{IC}$  of  $148 \pm 35 \text{ J/m}^2$ , while methacrylated oleic resins had a  $G_{IC}$  of  $110 \pm 15 \text{ J/m}^2$ . Fracture theories show that fracture properties decrease as the content of defects in the polymer network increase [31]. Because of the lower extents of cure of VE resins using oleic and linoleic acid monomers, there was a greater concentration of defects, which caused the fracture properties to be low. Yet, the fracture properties of fatty acid VE resins were greater than that of styrene-based VE resins ( $G_{IC} = 85 \pm 35 \text{ J/m}^2$ ). The reason for this has to do with the fact that

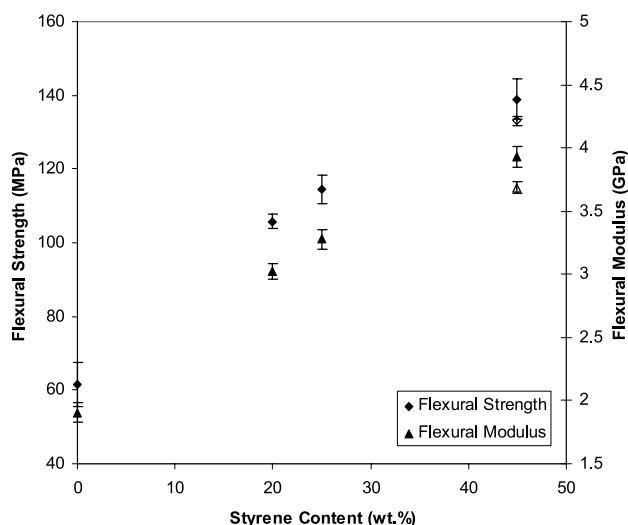


Fig. 8. The flexural strength and flexural modulus as a function of styrene content in the vinyl ester resin. The resins contain 55% vinyl ester monomers and 45% reactive diluent (styrene and MLau). The properties of Derakane 411-C50 are shown as open symbols.

vinyl ester monomers react to a fairly low extent (i.e. 70%) with styrene as the reactive diluent relative to when fatty acid monomers are used (i.e. 85%). Thus, there were fewer defects, such as dangling chain ends, in fatty acid resins. Furthermore, the fairly high content of unreacted free monomer in fatty acid resins ( $\sim 35\%$ ) acted as a plasticizer and toughened the polymer.

Ternary blends of VE, styrene, and fatty acid monomers produced polymers with better fracture properties than the binary counterparts, as shown in Fig. 9. This occurred because of a combination of fewer defects and higher moduli. The fatty acids allowed for high vinyl ester monomer conversion, while the styrene caused a high overall conversion, resulting in a lower content of dangling chain ends relative to the binary blends. Fracture theories, such as vector percolation, show that fracture properties increase with increasing modulus if the connectivity of the polymer is unaffected [32]. As shown previously, increasing the styrene content increased the rigidity of the ternary blends, therefore, causing an increase in the fracture properties.

#### 4. Conclusions

MFAs can be used as styrene replacements in vinyl ester resins because of their low viscosity, low volatility, low cost, and their ability to free-radically polymerize. However, judicious choice of the fatty acid monomer is needed. Unsaturation sites along the fatty acid backbone reduced the cure rate, monomer conversion, and polymer properties. Increasing fatty acid chain length also lowered the polymer properties and increased the viscosity by increasing intermolecular interactions. Therefore, short saturated

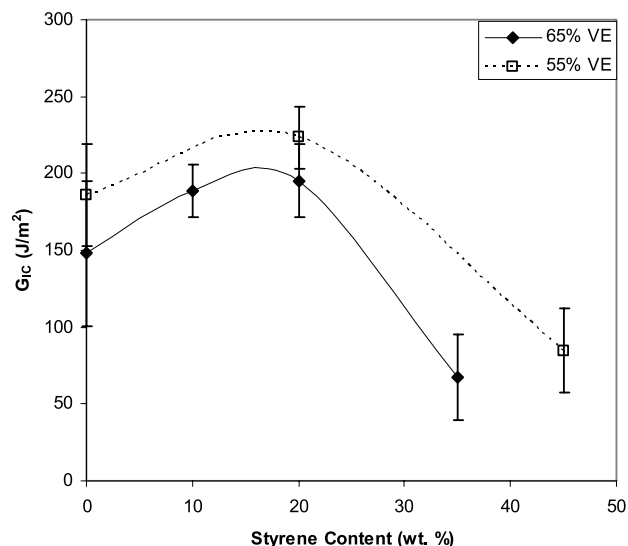


Fig. 9.  $G_{IC}$  of VE/MLau/styrene as a function of styrene content in the resin for resins containing 55 and 65 wt% VE 828.

fatty acids, such as lauric acid, are ideal fatty acids as styrene replacements in vinyl ester resins.

Vinyl ester resins using fatty acid monomers alone as the reactive diluent have properties that are slightly inferior to commercial VE resins. However, ternary blends of VE, FA, and styrene monomers have properties that are comparable to commercial resins. As a large advantage, these resins use less than half the styrene mass of commercial resins, thereby helping to reduce styrene emissions. In addition, the properties of VE resins can be improved by using fatty acids with shorter chain lengths. VE resins using methacrylated lauric acid as the primary reactive diluent with 10–20 wt% styrene is optimum for creating low VOC resins with low viscosity and high polymer properties.

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## References

- [1] Environmental Protection Agency. Fed Register 2003;68:19375–443.
- [2] Liu K. Soybeans: chemistry, technology, and utilization. New York: Chapman and Hall; 1997. p. 27–30.
- [3] Kirschenbauer HG. Fats and oils: an outline of their chemistry and technology. New York: Reinhold Publishing Corp; 1960. p. 146–56.
- [4] Bunker SP, Wool RP. J Polym Sci, Part A: Polym Chem 2002;40: 451–8.
- [5] Wool RP, Kusefoglu SH, Palmese GR, Zhao R, Khot SN. US Patent, 6,121,398; 2001.
- [6] Khot SN. Synthesis and application of triglyceride based polymers. Dissertation. Newark: University of Delaware; 2001.
- [7] Khot SN, La Scala JJ, Can E, Morye SS, Williams GI, Palmese GR, Kusefoglu S, Wool RP. J Appl Polym Sci 2001;82:703–23.
- [8] Malik M, Choudhary V, Varma IK. Rev Macromol Chem Phys 2000; C40:139–65.
- [9] Product Bulletin for Aerojet Accelerator, AMC-2. Rancho Cordova: Aerojet Chemicals; 2000.
- [10] ASTM D1980–1987. Annual book of ASTM standards, vol. 08.01. West Conshohocken, PA: ASTM; 1987. p. 428–29.
- [11] Pouchert CJ, editor. The Aldrich library of infrared spectra. 3rd ed. Milwaukee: Aldrich Chemical Co; 1981.
- [12] Brill RP, Palmese GR. J Appl Polym Sci 2000;76:1572–82.
- [13] Garcia AA, Bonen MR, Ramirez-Vick J, Sadaka M, Vuppu A. Bioseparation process science. Malden: Blackwell Science; 1999. p. 181–3.
- [14] Palmese GR, La Scala JJ, Sands JM. Vinyl ester monomers to reduce emissions and toughen polymers, US Provisional Patent; April 2004.
- [15] Macosko CW. Rheology: principles, measurements, and applications. New York: Wiley; 1994. p. 188–205.
- [16] Ziaee S, Palmese GR. J Polym Sci, B: Polym Phys 1999;37:725–44.
- [17] Nielsen LE, Landel RF. Mechanical properties of polymers and composites. New York: Marcel Dekker; 1994. p. 140–2.
- [18] Palmese GR, McCullough RL. J Appl Polym Sci 1992;46:1863–73.
- [19] Strobl G. The physics of polymers, 2nd ed. New York: Springer; 1997. p. 301–24.
- [20] ASTM D790–92. The physics of polymers, vol. 08.01. West Conshohocken, PA: ASTM; 1992. p. 155–62.
- [21] ASTM 5045–93. The physics of polymers, vol. 08.03. West Conshohocken, PA: ASTM; 1993. p. 307–15.
- [22] La Scala JJ. The effects of triglyceride structure on the properties of plant oil-based polymers. Dissertation. Newark: University of Delaware; 2002.
- [23] Guo A, Cho Y, Petrovic S. J Polym Sci, Part A: Polym Chem 2000;38: 3900–10.
- [24] Gunstone FD. An introduction to the chemistry and biochemistry of fatty acids and their glycerides. Bungay, Great Britain: Chapman and Hall; 1967. p. 14.
- [25] Malik M, Choudhary U, Varma IK. Rev. Macromol. Chem. Phys. 2000;C40:139–65.
- [26] Ashbee KHG. Fundamental Principles of Fiber reinforced composites, 2nd ed. Lancaster: Technomic Publishing Co., 1993. pp 33–80.
- [27] Odian G. Principles of polymerization, 2nd ed. New York: Wiley; 1981. p. 250–1.
- [28] Hendrana S, Hill DJT, Senake Perera MC, Pomery PJ. Polym Int 2001;50:597–605.
- [29] Greenley RZ. Free radical copolymerization reactivity ratios. In: Brandrup J, Immergut EH, Grulke EA, editors. Polymer handbook. 4th ed. New York: Wiley; 1999. p. II/182–II/288.
- [30] Product Bulletin for Dow Derakane. Midland: Dow; 2000.
- [31] Wool RP. Polymer interfaces, structure, and strength. New York: Hanser Publishers; 1995. p. 102–16.
- [32] Sieradzki K, Li R. Phys Rev Lett 1986;56:2509–12.

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